This presentation does not contain any proprietary, confidential, or otherwise restricted information

Active, Tailorable Adhesives for Dissimilar Material Bonding, Repair, and Assembly

Dr. Mahmoodul Haq[1] and Dr. Lawrence T Drzal[2]

[1] Assistant Professor, Civil & Environmental Engineering

[2] University Distinguished Professor, Chemical Engg. & Material Science

Composite Vehicle Research Center (CVRC)

Michigan State University

Project ID # : LM087

MICHIGAN STATE UNIVERSITY | Composite Vehicle Research Center

OVERVIEW

TIMELINE

- **Start Date:** October 1, 2013
- **End Date:** March 31, 2016
- Percent Complete – 100%

BUDGET

- **Total Project Funding:** $599,999
- **Funding Received in Budget Period 3: (01/2016 – 03/2017) :** $236,629
- **Funding for Budget Period 4:**
  - End of Project - $0

BARRIERS ADDRESSED

- **Joining and Assembly**
  - **Light-weight, reversible bonded joints**
- **Performance**
  - **Enhanced damage resistance of joints using nanoparticles**
- **Predictive Modeling Tools**
  - **Development of Experimentally Validated Simulations.**

Partners / Collaborations

- **Eaton Innovation Center, MI.**

Project Lead

- **Michigan State University, Composite Vehicle Research Center (CVRC).**

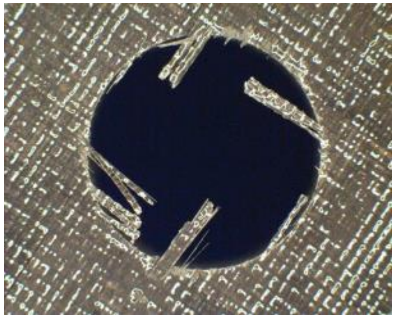
Introduction / Relevance - Joining

- **JOINING / ASSEMBLY**

➢ Joining is inevitable, allows versatility in assembly and repair, reduces costs and time.

➢ Considered a 'weak-link' in the structure due to complex phenomena & interactions.

- ***Mechanical Fastening***
- ***PROS: a) Repair and Re-assembly, b) confidence in use as it is commonly used***
- ***CONS : a) Adds Weight, b) machining holes, c) delamination in composites, d) stress-concentrations***



Delamination in composites due to hole-drilling, Gardiner, Composites World , (2012)

- ***Adhesive Bonding***
- ***PROS: a) Light Weight and b) load distribution over larger areas***
- ***CONS : a) permanent joint (cannot be repaired or re-assembled), b) lack of confidence in common use to reliability of bonding.***

Examples of Adhesive Joints
a) Lap-Joint , b) Double Lap-Joint

There is a Need for a JOINING TECHNIQUE that can INHERIT the MERITS of BOTH bolted & bonded techniques while still being compatible with current assembly line practices

Introduction / Relevance - Joining

RELEVANCE:

Key Technical Gaps for Systems for Light-Duty Vehicles

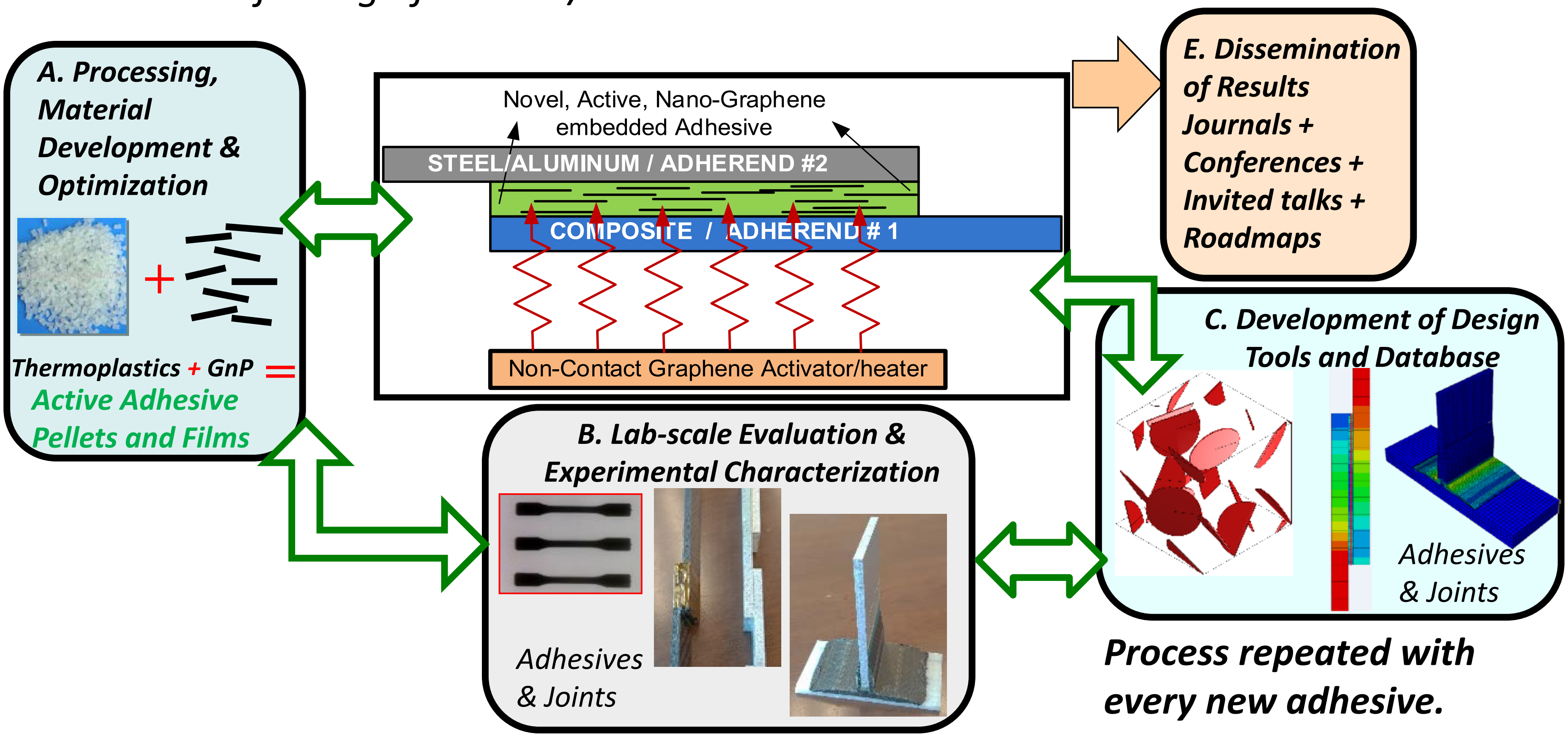
System	Three Most Significant Technical Gaps Impeding Widespread Implementation		
Body Structures (Composites)	Lack of understanding of properties with respect to fracture and energy absorption	Lack of predictive engineering and modeling tools	Lack of high-volume manufacturing capability
Body Structures (Metals)	Lack of technology for joining dissimilar materials	Properties of alternative lightweighting materials are inadequate for forming and energy absorption	Modeling, simulation, and design tools are inadequate for optimization
Chassis and Suspension	Inadequate properties (strength, ductility, corrosion resistance, etc.)	Manufacturing capacity to produce high- integrity components is inadequate	Robust joining processes, especially to other materials, are lacking
Closures, Fenders, and Bumpers	Fast and reliable processes for joining dissimilar materials are not available	Design knowledge and databases are inadequate	Cost/availability of most lightweight materials and current manufacturing processes are not competitive
Engines and Transmissions	Materials needed for advanced technology propulsion systems are not cost competitive	Properties of current materials are not adequate	Databases for modeling and design are inadequate

Source: http://www1.eere.energy.gov/vehiclesandfuels/pdfs/wr_ldvehicles.pdf

This project address three concerns on : a) joining dissimilar materials, b) experimentally validated simulations and c) joining techniques relevant and capable of easy transition to industrial applications

Summary of Progress : Objective, Approach, Relevance, Milestones and Accomplishments

- ***OBJECTIVE:*** *To demonstrate the feasibility of 'ACTIVE Adhesive' technology for structural joining of similar / dissimilar substrate materials.*



Process repeated with every new adhesive.

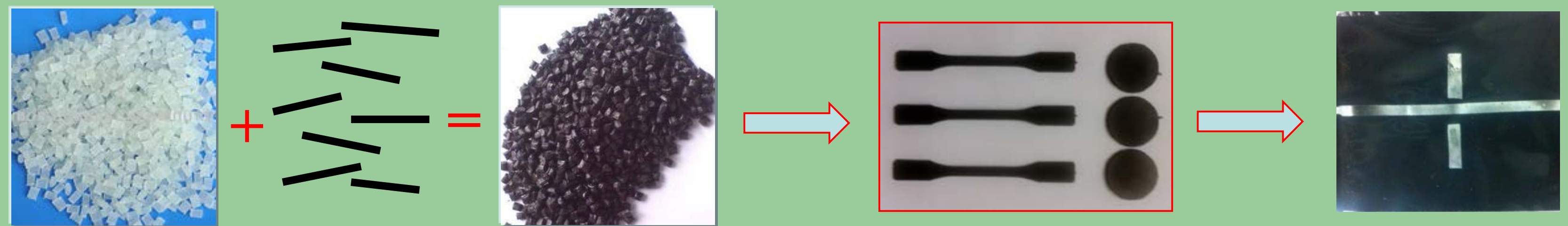
- **APPROACH:** An integrated experimental and numerical computational materials (materials by design) based approach. Multi-use, Repair & Reassembly?

Summary of Progress :
Relevance, Milestones and Accomplishments

	Milestone	Type	Description	Status
FY 14	Activation and Bonding	Technical	The novel active adhesive couples with microwave radiations to activate, bond/un-bond resulting similar joints	SUCCESS!!
	Structural Properties Defined	Go / No-Go	The novel active adhesive structural properties (lap-shear) pre- and post- exposure to corrosive environments is better or equal to requirements in industrial practices with conventional bonding techniques	SUCCESS! GO ☑
FY 15	Demonstration of Structural Properties	Technical	The structural properties (lap-shear) pre- and post- exposure to corrosive environments is better or equal to requirements in industrial practices with conventional bonding techniques	SUCCESS!!
	Proven Efficiency	Technical	The NDE techniques used can prove the efficiency of the activation and re-assembly/bonding of the resulting joints	SUCCESS / In-Progress
	Characterization of Material Properties	Go / No-Go	The experimental characterization of material properties of the adhesive and adherend can be successfully performed to provide input to robust simulations (next phase)	SUCCESS / In-Progress GO ☑
FY16	Model Using Simulations	Technical	The simulations developed model the behavior and failure phenomena accurately without making crude assumptions and successfully agree with a wide range of experimental tests. <u>NOTE: Experimentally Validated Simulations!</u> An effort of 50% or more will be on experiments to validate and increase the robustness of the models, and to create reliable databases.	*SUCCESS !* *Large-scale components & Environmental Testing*

Progress: Active Adhesives – Hybridization of GnP particles

RECAP: SCHEMATIC PRODUCTION OF ACTIVE ADHESIVES



Thermoplastic + *GnP* = *Active Adhesive Pellets* → *Injection molded discs* → *Adhesive films + spacers*

MATERIALS USED:

Substrates:

- Aluminum
- Steel
- CFRP
- GFRP

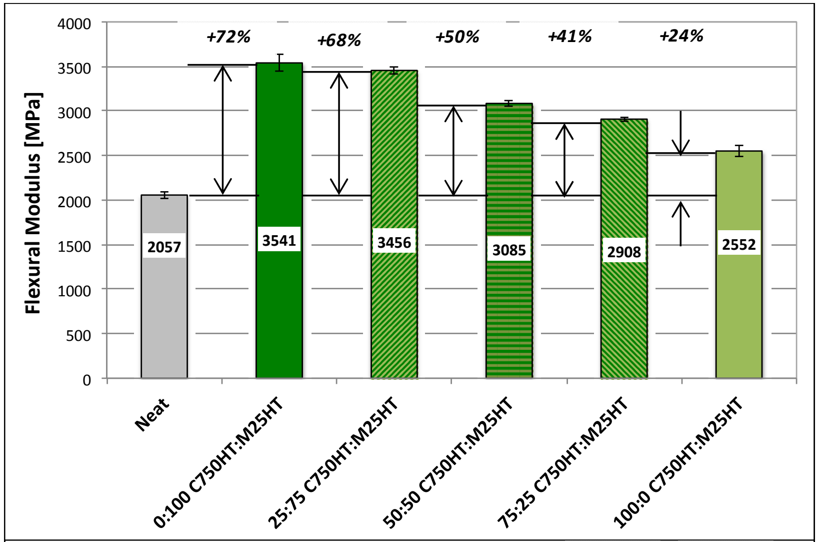
TP Adhesives:

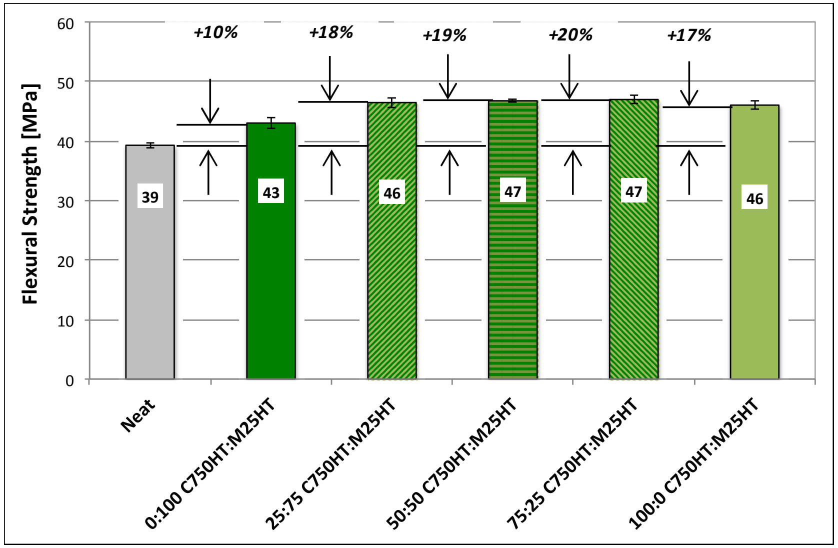
- Nylon-6
- Polycarbonate
- Polyolefins
- ABS
- **HIPS(current)**

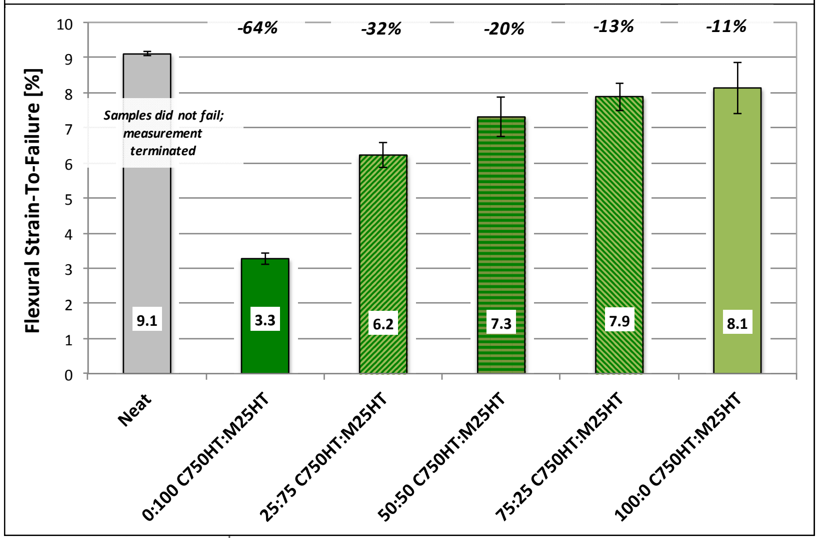
- **HIPS** (High Impact poly styrene) thermoplastic was pursued as ABS adhesive showed relatively "slower" activation with microwave
- **GnP hybridization**: Mixing larger size particles (M25HT) with smaller size particles (C750HT), but **WHY?**
    - Increase percolation, better interconnected GnP network
    - Reduce loss in strengths by minimizing the stress-concentration due to large particles
- **NEXT:** Effect of Hybridization on Mechanical Properties and activation

Progress: Technical Accomplishments/Results
Effect of GnP Hybridization

Flexural Properties of HIPS (7.5wt%) with GnP Hybridization C750HT:M25HT



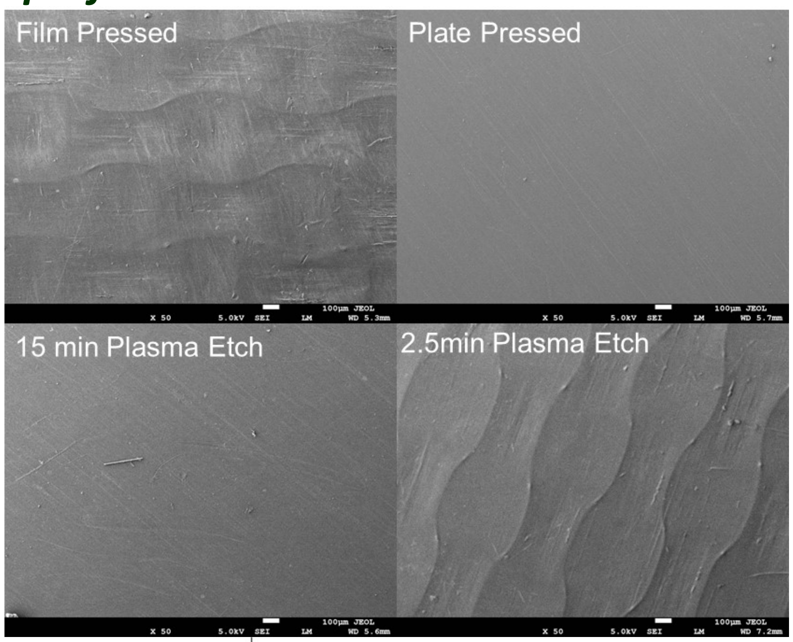




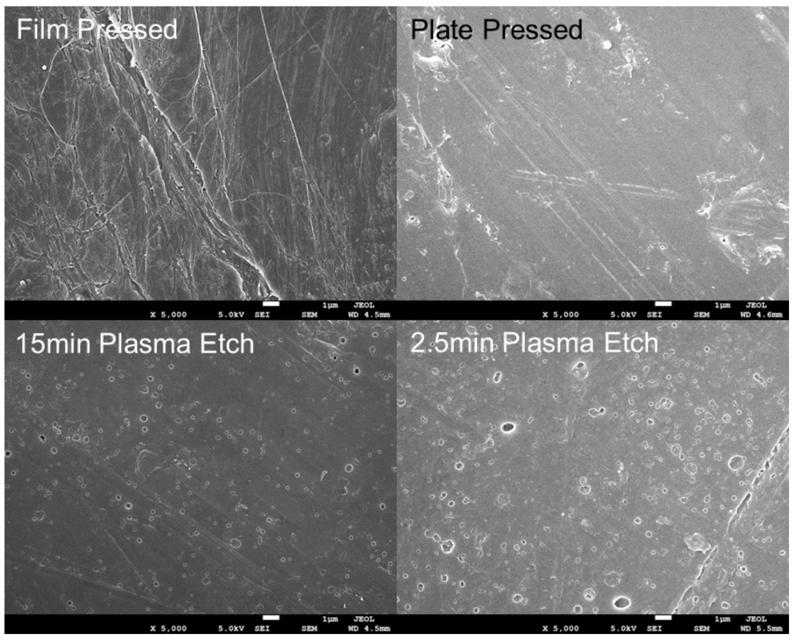
- ***M25HT shows highest increase in modulus; modulus increase decreases with increasing C750HT concentration***
- ***Flexural strength increase appears constant above 25wt% C750HT***
- ***Strain to failure increases with increasing C750HT concentration and is statistically similar above 50wt% C750HT***
- ***KEY is SYNERGY and TAILORABILITY***
- ***Similar results were obtained for tensile & impact behaviors, for brevity not discussed here.***

Progress: Technical Accomplishments/Results
Surface Prep and Lap-Shear Testing

- ***Most commercial thermoplastics are designed for injection molding applications and contain a proprietary "release agent" for ease in removal of finished parts.***
- ***Obtaining 'active adhesives' films by pressing the film in between release plies also effects surface adhesion***
- ***This leads to interfacial failures of multi-material joints.***
- ***Surface treatment of adhesive, namely exposing the adhesive films to O_2 plasma was performed to overcome this issue***

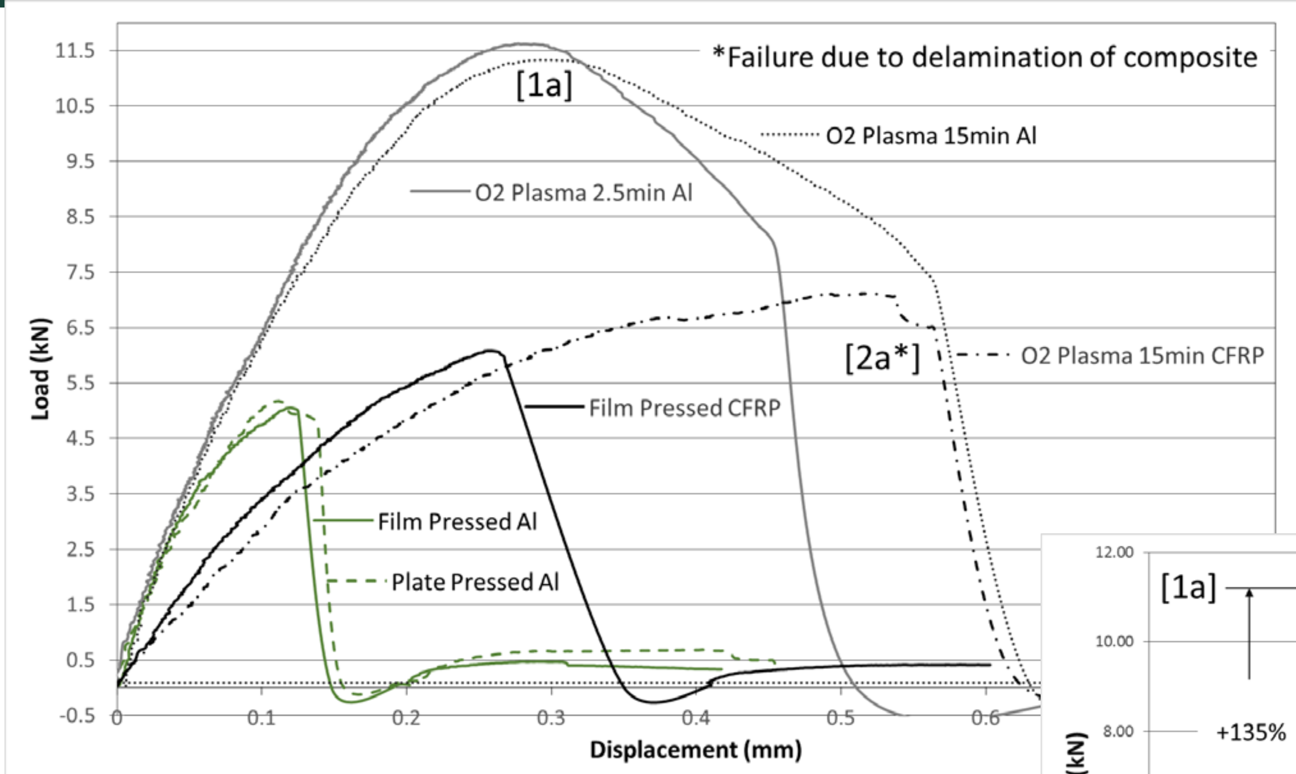


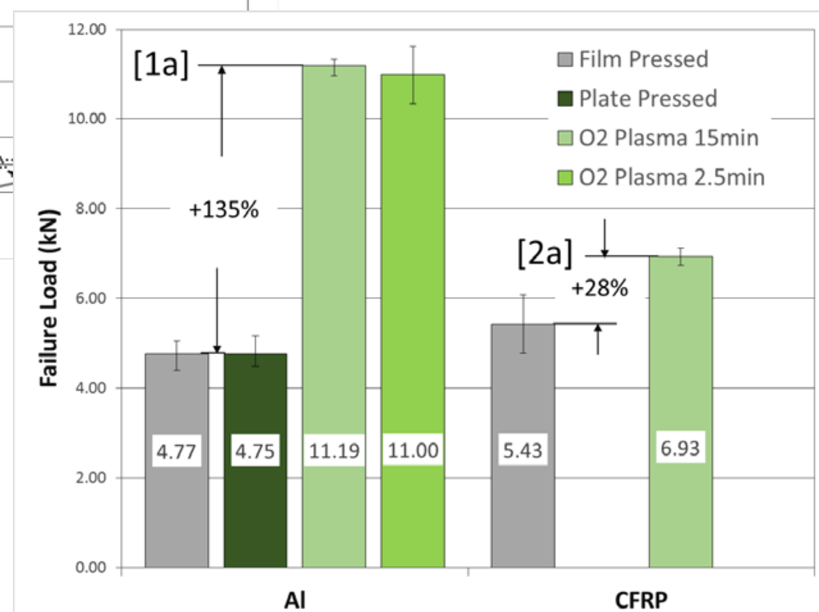
@ 50x

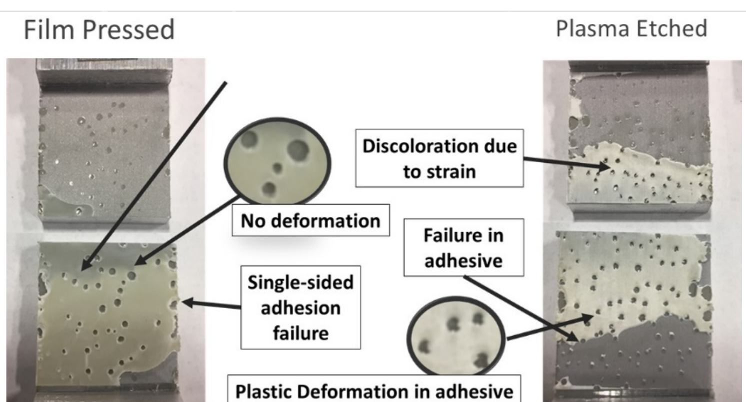


@ 5000x

Progress: Technical Accomplishments/Results
Surface Prep and Lap-Shear Testing



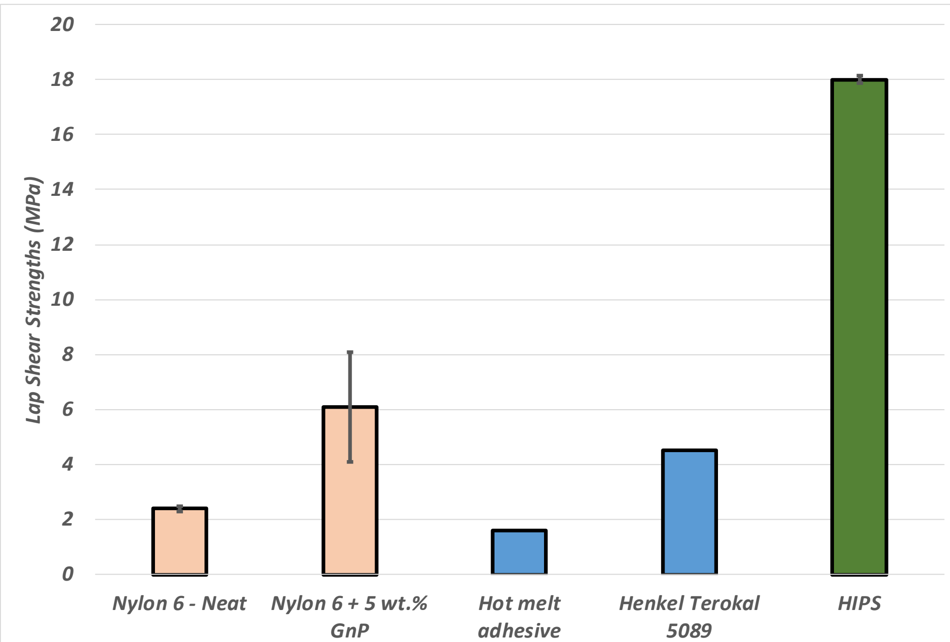




MICHIGAN STATE UNIVERSITY

Progress: Technical Accomplishments/Results Surface Prep and Lap-Shear Testing

Comparison of Lap Shear Strengths of similar class of materials



General thumb rules for Lap Shear Strengths of epoxies and structural adhesives [3,4]:

EPOXIES

HIGH: 2500-4000 psi (17.0 – 28.0 MPa)

AVG : 1200-1900 psi (8.2 – 13.0 MPa)

LOW : <800 psi (< 5.5 MPa)

Structural Tapes[4]: 5.0 - 13.5 MPa

Cyanoacrylates[4]: 7.0 – 20.0 MPa

Acrylics[4]: 14.0 – 28.0 MPa

HIPS (shown on left): ~18.0 MPa

- ***Lap-shear joint strengths of plasma treated HIPS adhesive <u>far exceeds</u> those of similar class of thermoplastics and structural tapes, and more importantly are comparable to cyanoacrylates, acrylics and epoxies [3,4].***

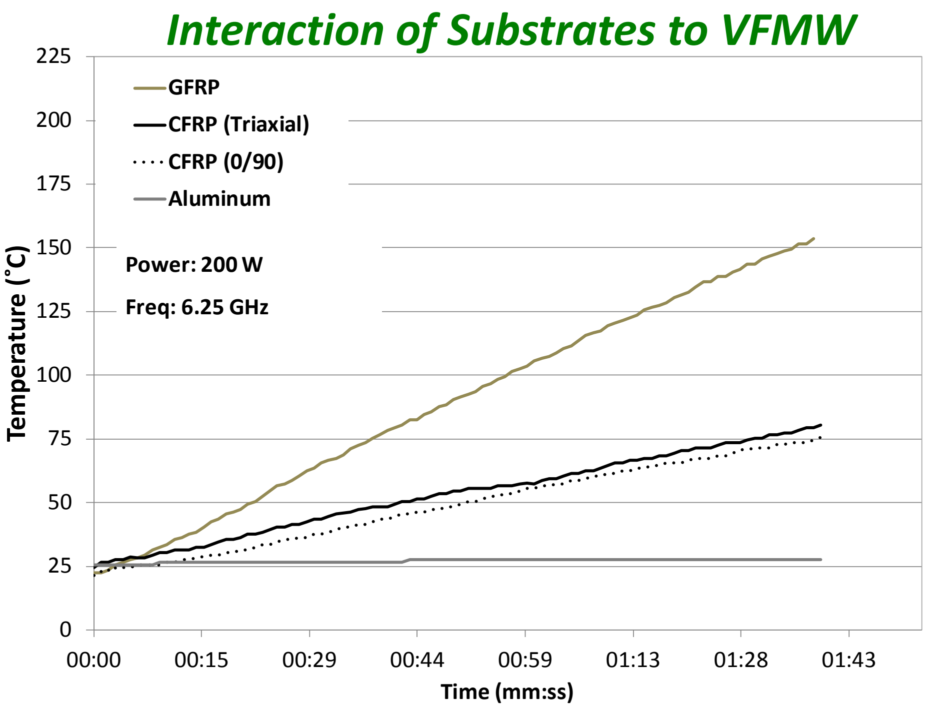
[1] Verna E, Koricho EG, Cannavaro I, Brunella V, Belingardi, G, Roncato D, Martorana B, Lambertini V, Neamtu VA, Ciobanu R, Adhesive joining technologies activated by electro-magnetic external trims, International Journal of Adhesion and Adhesives, 2013:46;21-25

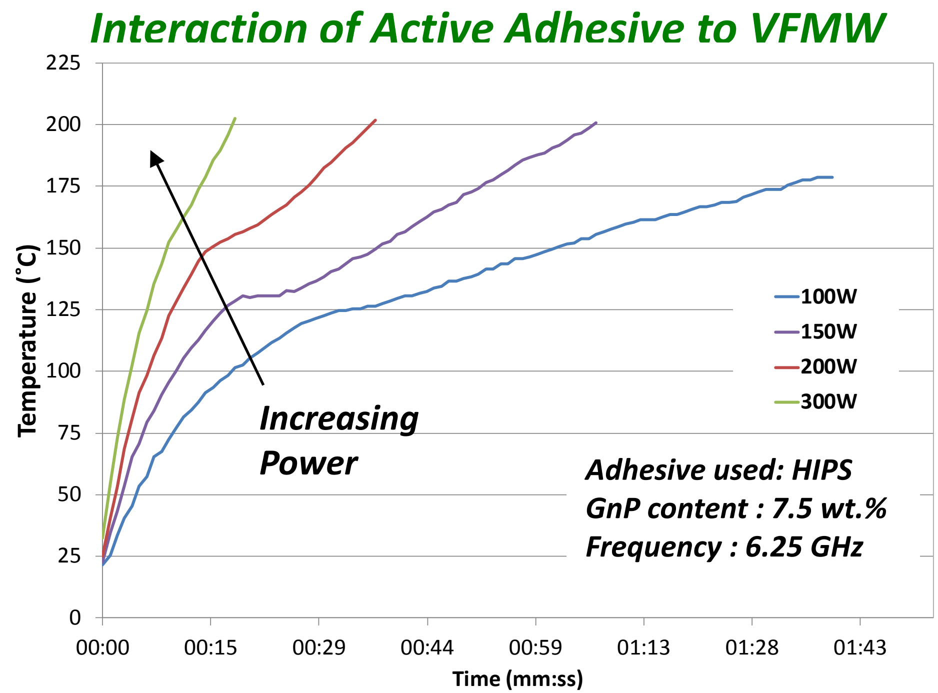
[2] X.Yang, L. Yao, Yong Xia, Qing Zhou, Effect of base steels on mechanical behavior of adhesive joints with dissimilar steel substrates, Int. J of Adhes. Adhesives, 2014;51:42-53

[3] Adhesive application guide, page 26, Epoxy Technology Inc., epotek.com, accessed 05/05/2017

[4] *Shari Loushin, 3M | Dec 01, 2016. "Choosing and Using Structural Adhesives." Machine Design. N.p., 08 Mar. 2017.*

Progress: Technical Accomplishments/Results
Targeted Heating of Adhesives





- ***Active adhesives heat much faster than substrates***
- ***Heating is accelerated with increasing GnP content and increasing Power***
- ***Aluminum and CFRP smooth surfaces seem to reflect/absorb microwave radiations and hence do not seem to heat up faster.***
- ***The joint arrangement/placement in the VFMW should be optimized to ensure activation of adhesive without reflection in substrates***

Progress: Technical Accomplishments/Results
Large-scale components

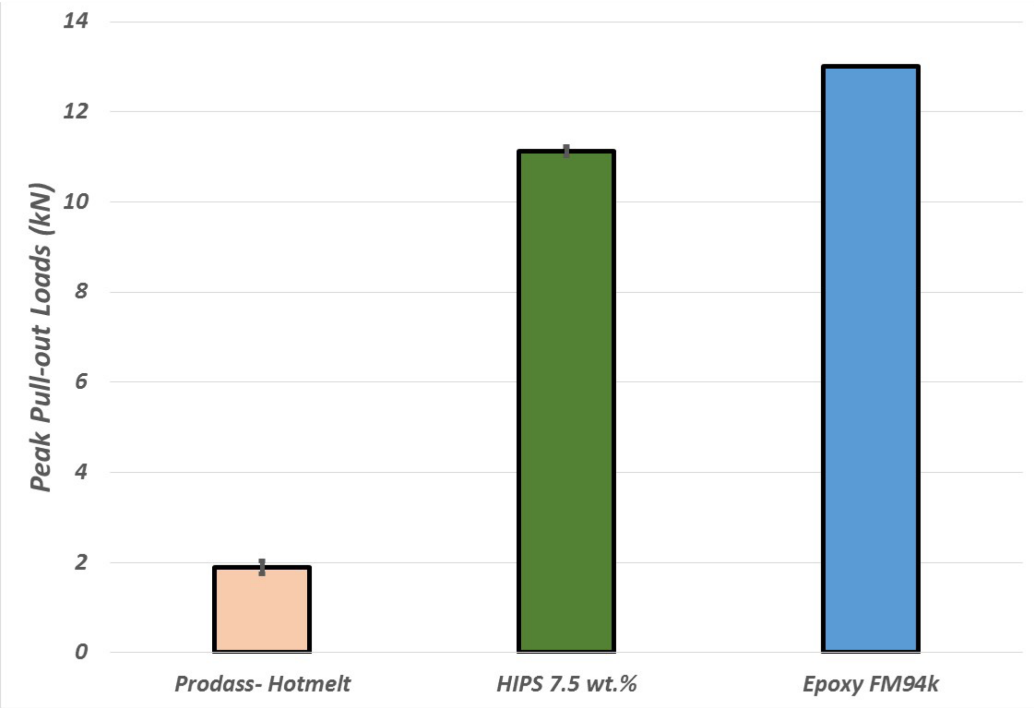
Aluminum rotor bonded to Steel Shaft using HIPS adhesive

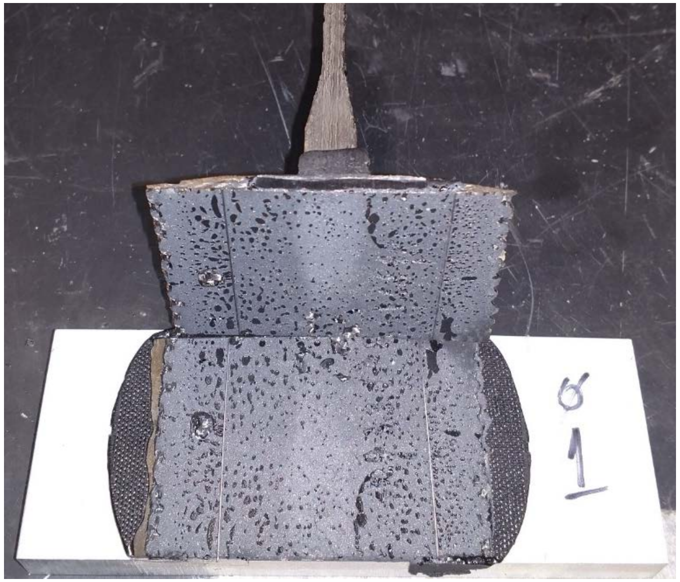
Carbon web bonded with 3D woven carbon preform and aluminum base using HIPS adhesive containing 7.5wt.% GnP

Typical Pi-/T-joint pull-out test setup

Progress: Technical Accomplishments/Results Large-scale components

Peak Pullout loads of Multi-material Pi/T-joints

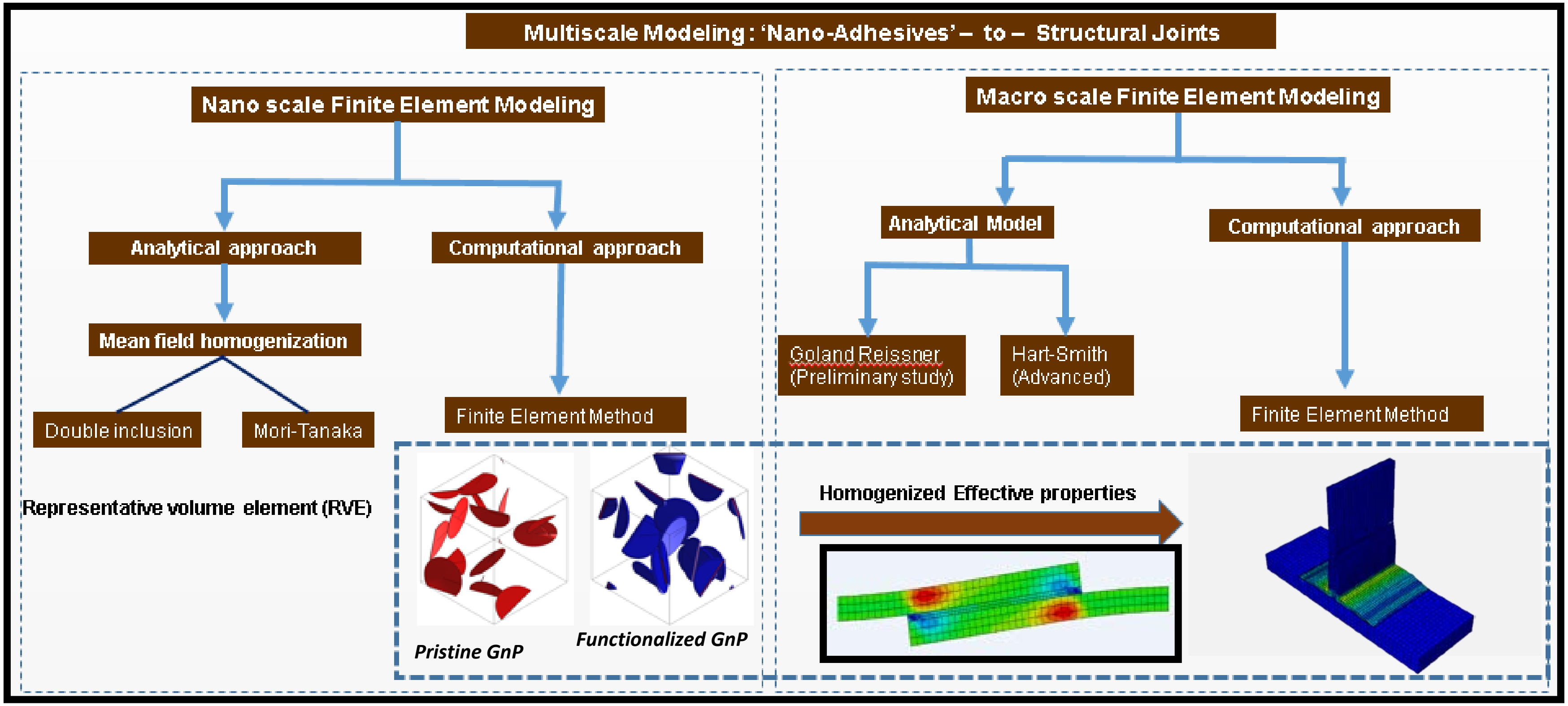




Cohesive failure of HIPS adhesive

- ***Peak Pull-out loads with active adhesives (HIPS 7.5 wt.%) superior than similar class of hotmelt adhesives and comparable to commercial epoxy (Cytec FM94k)***

Progress: Technical Accomplishments/Results Overview & Approach in Modeling



Study of adhesive characterization

- Effective stiffness, toughness, thermal & electrical conductivity.

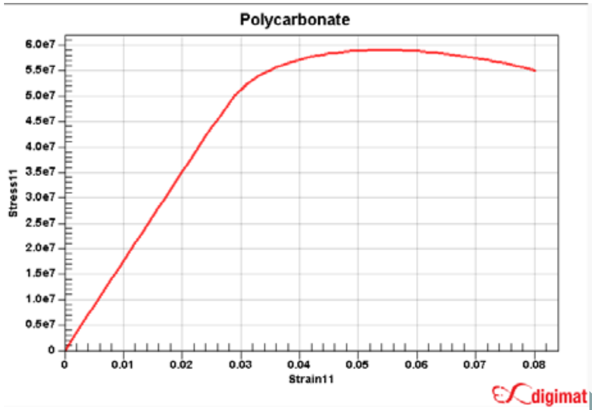
Study of Multi-material joining

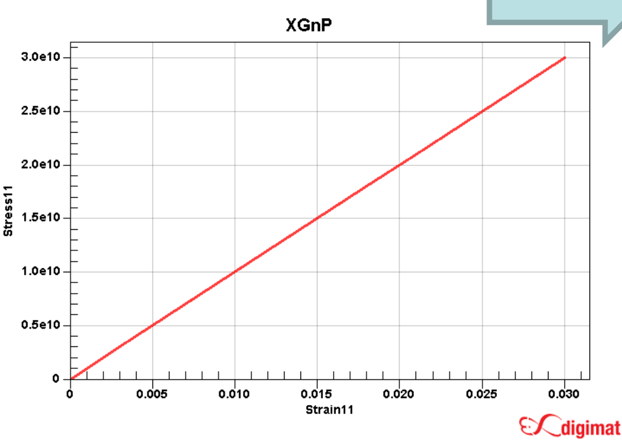
- Structural behavior, modeling damage/failure, progressive damage and development of experimentally validated simulations (EVS)

➢ ***Experimentally Validated Nano-scale models to help predict the structural behavior beyond the experimental matrix in this study***

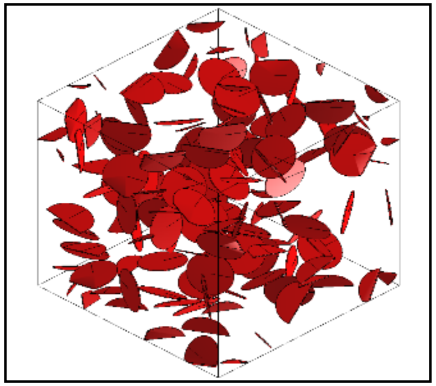
Progress: Technical Accomplishments/Results
Nano- / Micro- Scale Modeling

Material Models

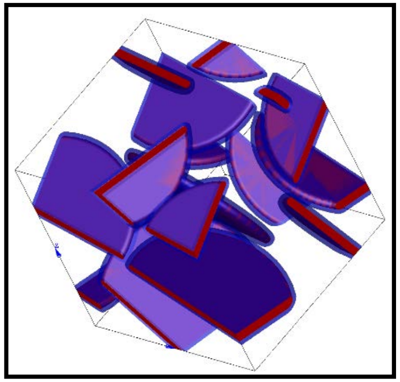




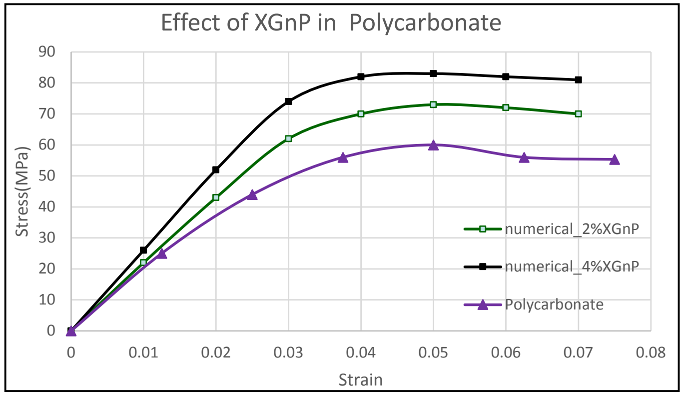
Unit Cell / Realistic MODELING



Microstructure of 2 wt.% Pristine GnP in Polycarbonate



Microstructure of 2 wt.% functionalized GnP in Polycarbonate

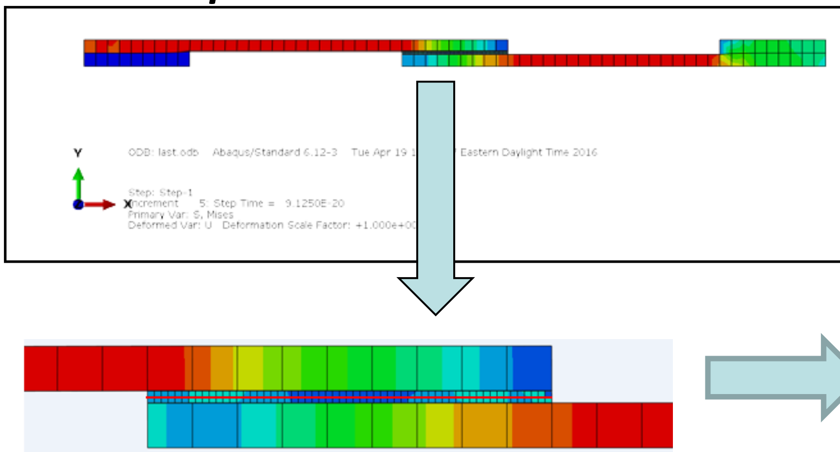


Prediction of Adhesive behavior with XGnP

- ***Realistic modeling and successful prediction of <u>nonlinear behavior</u>***
- ***Successful modeling of GnP/polymer interfaces to take functionalization into account.***
- ***Material model can be directly <u>input to structural models</u> or can <u>linked as multi-level models</u>***

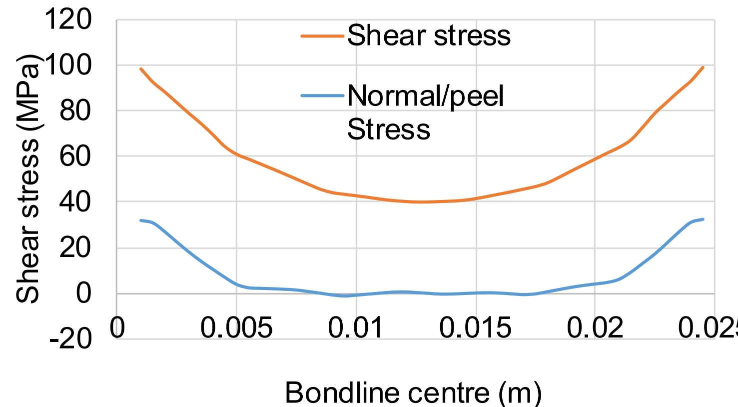
Progress: Technical Accomplishments/Results
Numerical Modeling – Lap Joint

- ***Adhesive Material Model from Nano-scale input into structural models***

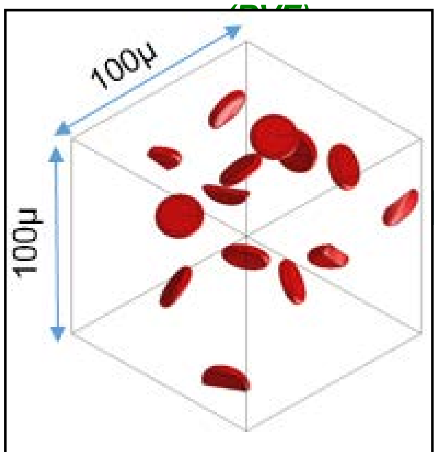


Previous work on numerical models capture:

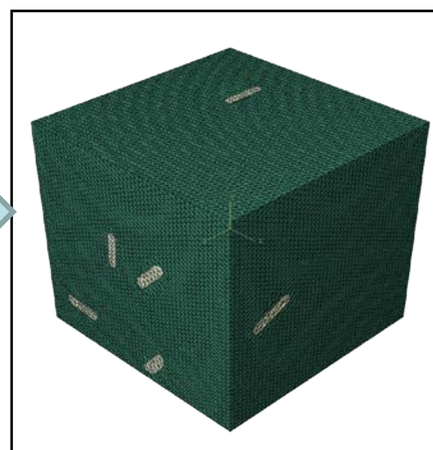
- ***GnP increases stiffness of adhesives***
- ***Clear effect on reduction of peel stresses.***
- ***Further progress on multi-scale modeling***



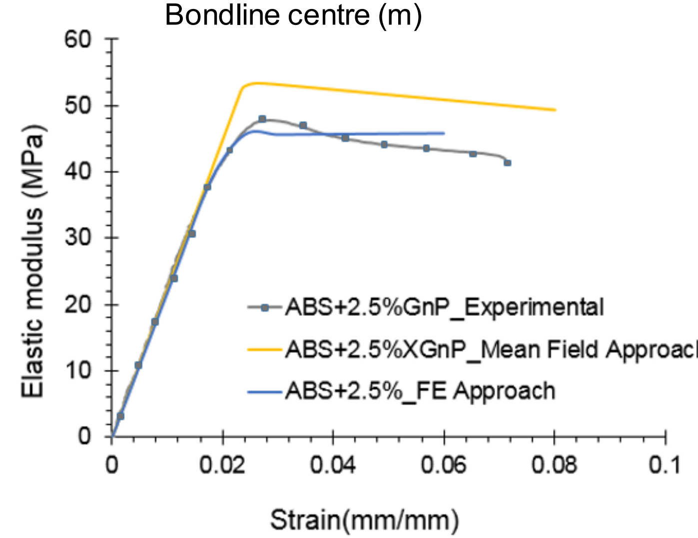
Representative Volume Element



FE Model



Validation: Comparison with Test results



Response to Previous Year Reviewers' Comments

Reviewers' Comment	Action Taken, Results and Comments
#1. The reviewer said that the overall approach is excellent. This is exciting fundamental work that will have far reaching impact on the composites re-engineering. The reviewer suggested studying the temperature inside the microwave with and without graphene and accordingly make a work plan to engineer the chemistry. The reviewer also suggested investigating the time dependency of melting the adhesive with & without GnP so as to learn the impact of graphene on the bondability of the synthesized adhesive.	The reviewers' observations and suggestions are accurate, excellent and appreciated. The investigators have worked considerably on enhancing the tailorability/reversibility of active adhesives without sacrificing the mechanical properties. Hybridization/mixing of larger and smaller GnP particles provides a "well-connected" network that enables rapid heating with VFMW while enhancing stiffness without losing strength.
#2. The reviewer stated … (positive feedback)… … but the project only has one year left and that is very little time to get an automobile manufacture or their suppliers directly involved where they will accept the technology and process being developed.	The investigators agree with the reviewers comments and feedback. The broader impact and the attention received in this project has initiated communications from auto industry. The investigators have toured assembly lines of major auto companies and obtained feedback to tailor our project. Also, investigators are pursuing research projects with American chemistry council and US Army TARDEC/NCMS/PPG on applying the lessons learned.
#3. The reviewer explained that the plan for future work includes corrosion studies, optimization work on processing, thermal testing, re-assembly and repair work, and efforts in NDE. The reviewer commented that additional evaluation on commercialization methods for large automotive applications would be beneficial for this type of joining method.	The reviewers' observations are accurate. The integration of NDE has improved the accuracy of the numerical models. Furthermore, the lack of confidence on bonded joints by the automotive industry can be overcome by integrated and rapid NDE.
#4. The reviewer said that the resource levels for this work appear appropriate for this project. Additional work and a future project(s) could branch from this work.	The investigators completely agree with the reviewer. The investigators look forward to working with industry and DOE in translating the volume of knowledge from this project into applications

Collaborations & Coordination

Collaborators / Partners	Details
Eaton Corporate Research and Technology **(PARTNER)**	✓Low-inertia, light-weight, supercharger applications ✓High-speed rotational/torsional testing ✓Non-destructive Evaluation at high speeds ✓Metal – to- metal and Metal to composite Bonding ✓In-situ repair, assembly and disassembly
U.S. Army TARDEC **(In-kind Collaborator)**	✓Periodic review of progress and guidance on relevant materials for automotive applications and path forward.
OakRidge National Laboratory **(ORNL)**, Carbon Fiber Technology Facility **(CFTF): (In-Kind Collaborator)**	✓Low-cost, Large-Tow Carbon Fiber. ✓Guidance of possible automotive applications

Barriers and Solutions + Future Work

- **CHALLENGES / BARRIERS:**
- **"Proprietary" release agents in commercial thermoplastics designed for injection molding led to interfacial failures of multi-material joints. ADDRESSED: Surface treatment of adhesive film (plasma treatment) prior to bonding removed the release agent and significantly increased both the stiffness (peak load) and toughness (ductility) of the resulting joints.**
- **Microwave Equipment: The sample size is still limited by the size of the VFMW oven. POSSIBLE SOLUTION*: The use of other nanoparticles or hybridization of nanoparticles and use of other electromagnetic radiations (eddy currents) for activation is possible***

- ***FUTURE WORK (Wrapping Up and Dissemination):***
- ***Complete corrosion testing of multi-material joints and record the findings.***
- ***Record and statistically analyze the varying temperature testing of joints (as obtained from Eaton)***
- ***Dissemination of results (end of project report) and journal/conference publications.***

Summary

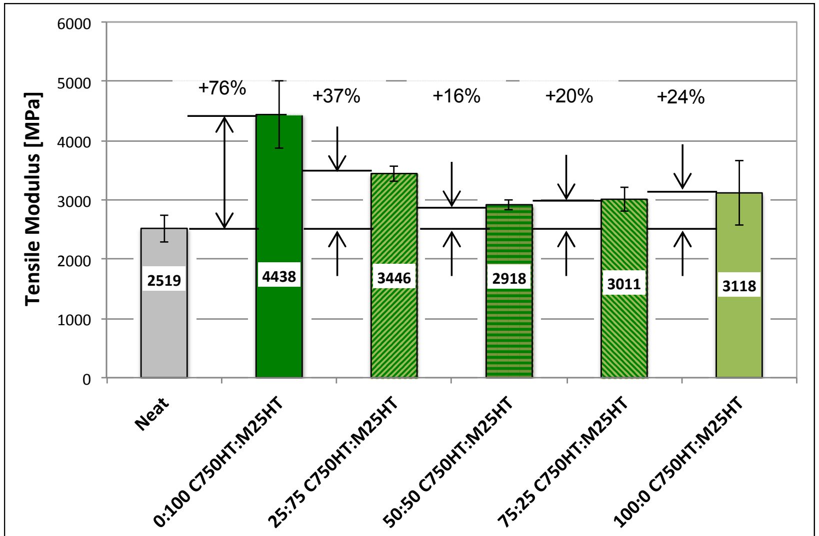
- **RELEVANCE:**
  - Joining & Assembly: Multi-material Joints that inherit the benefit of both bonded (lightweight) & bolted (re-assembly+repair) joints through 'active,' 'reversible,' adhesives.
- **APPROACH:**
  - Reinforcement of thermoplastic adhesive with novel graphene nano-platelets (GnP) and to use GnP/microwave-interaction for 'targeted heating of adhesive' thereby allowing ease of repair and re-assembly
  - An Integrated Experimental & Simulations based approach that eliminates the trial-and-error approach is adopted. Robust design tools are also developed.
- **KEY TECHNICAL ACCOMPLISHMENTS**
  - Targeted heating of adhesives, dis-bonding and re-assembly and "Healing" was proved Multi-materials, various adhesive and three types of joints successfully developed.
  - Surface treatment of adhesive films (high impact poly styrene, HIPS) prior to bonding leads to shear strengths that <u>significantly surpass</u> similar class of thermoplastics and structural tapes, and more importantly are <u>comparable to cyanoacrylates, acrylics and epoxies .</u>
- **Partners / Collaborations:** Eaton Innovation Center, MI.
- **FUTURE WORK:**
  - Document / complete corrosion and Elevated Temperature testing
  - Dissemination of Results and Findings
    - Reports, Journals, conferences and posters.

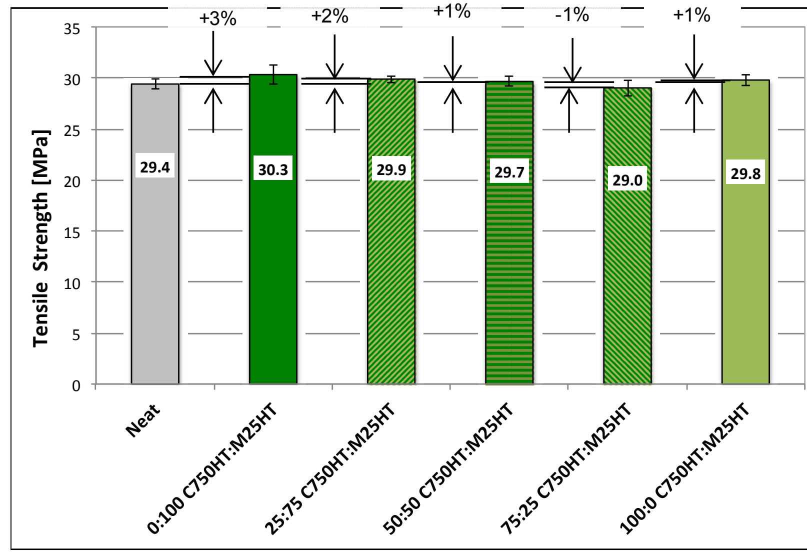
Active, Tailorable Adhesives for Dissimilar Material Bonding, Repair and Assembly

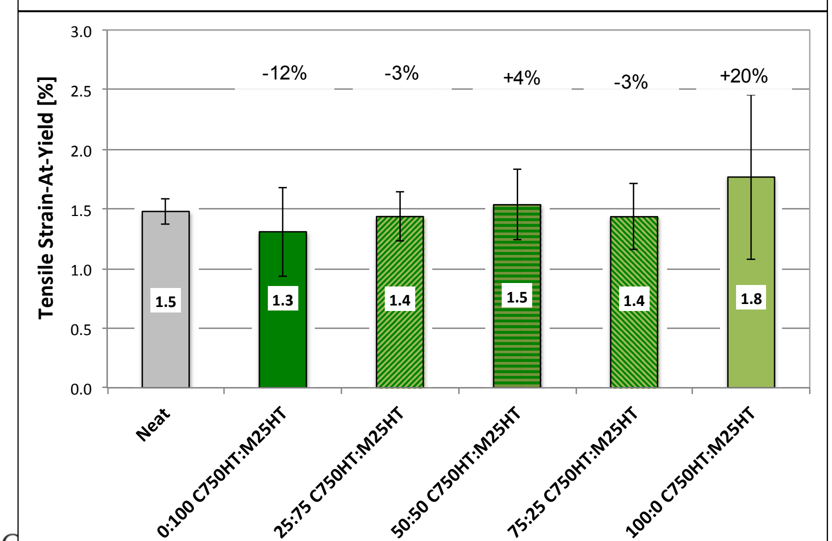
TECHNICAL BACKUP SLIDES

Progress: Technical Accomplishments/Results
Effect of GnP Hybridization

Tensile Properties of HIPS (7.5wt%) with GnP Hybridization C750HT:M25HT

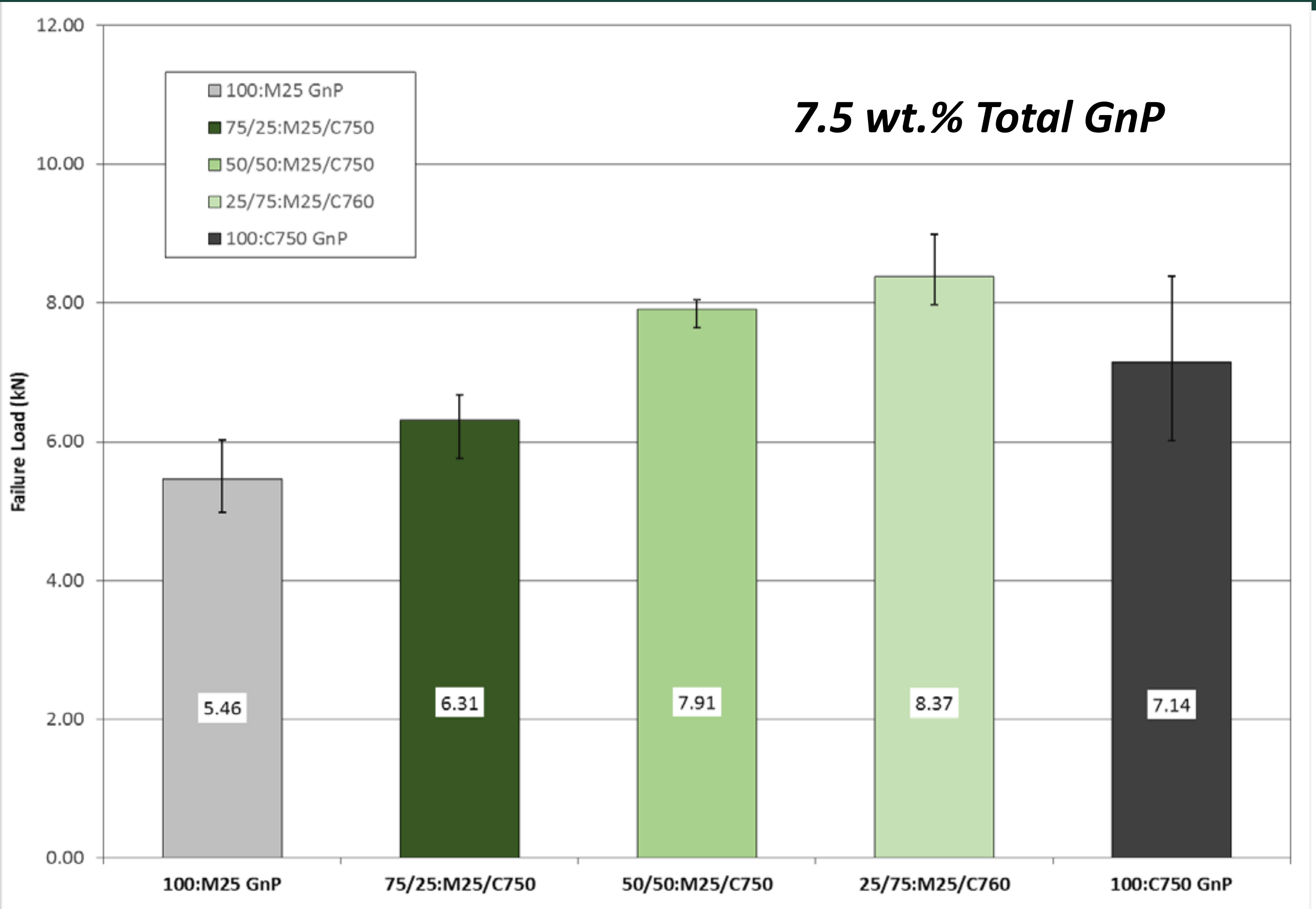






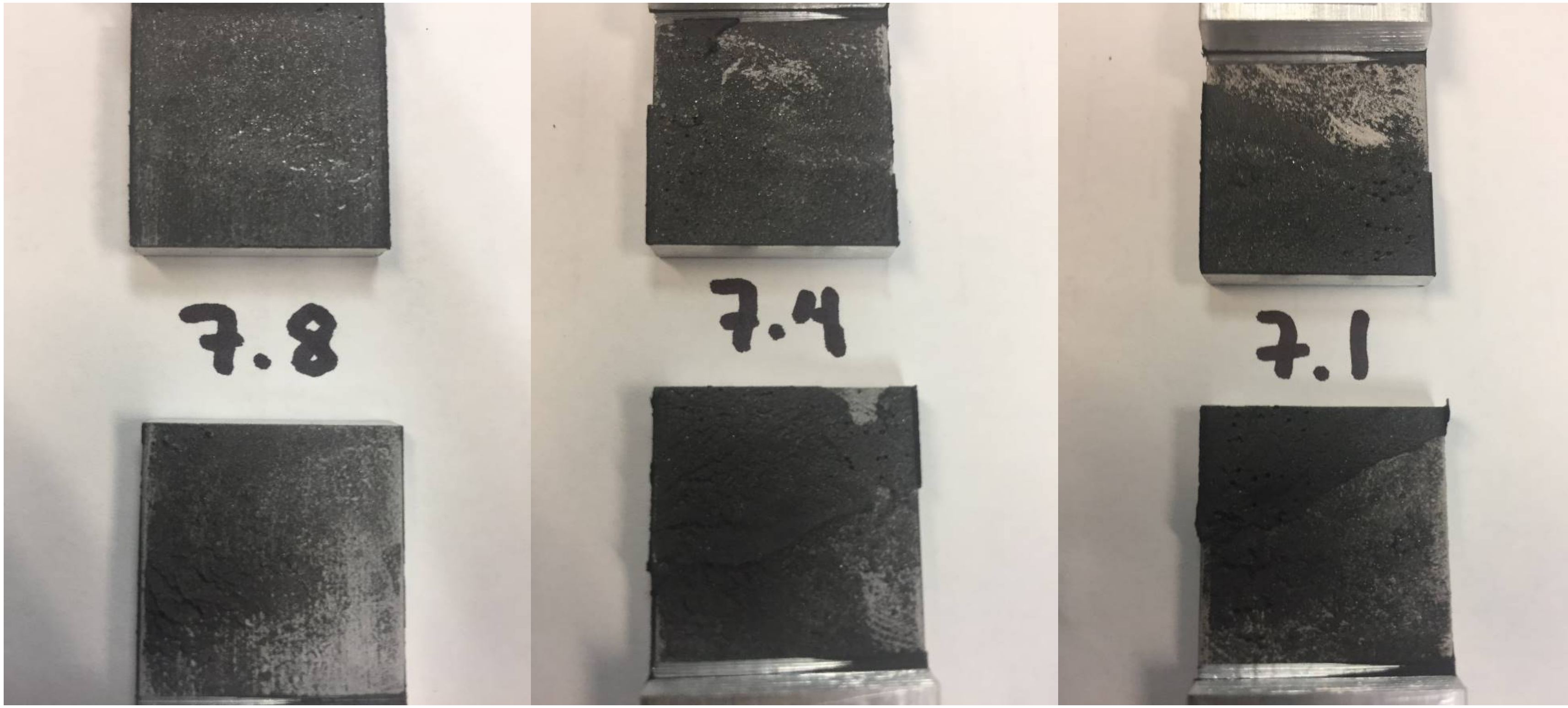
- ***M25HT shows highest increase in modulus; modulus increase decreases with increasing C750HT concentration and is statistically similar above 50wt% C750HT***
- ***Tensile strength is statistically similar for all GnP concentrations***
- ***Tensile strain-at-failure is statistically the same for all samples***

Effect of GnP Blending/Hybridization on Peak Lap-shear loads



- ***Synergy between the smaller and larger particles observed. Smaller particles reduce stress concentration and allow for a good percolation network. The larger particles provide better load transfer and stiffness improvement. The hybridization provides the best of stiffness and toughness***

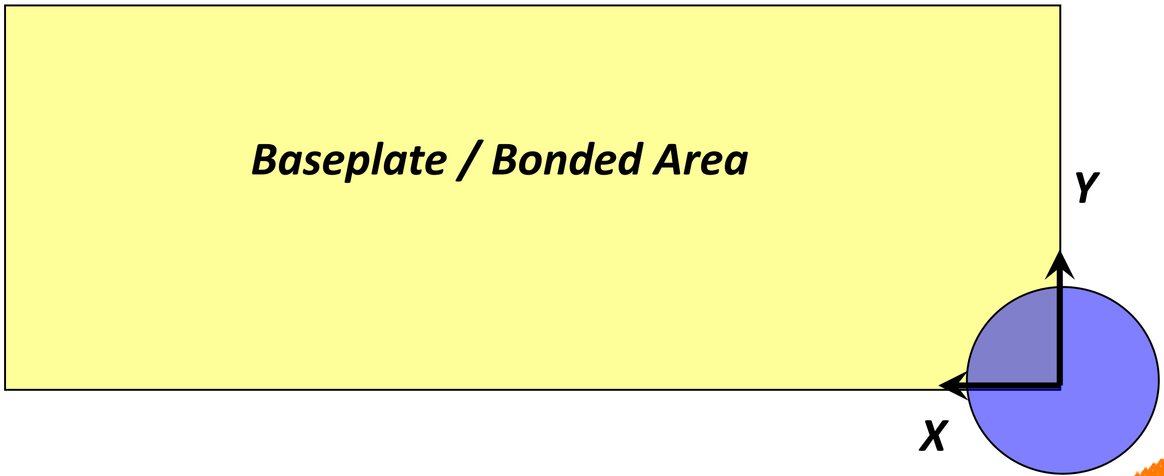
Lap Joint Fracture Surfaces
HIPS adhesive, plasma treated

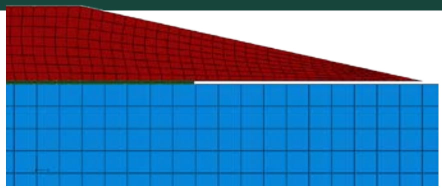


75/25:M25/C750	50/50:M25/C750	25/75:M25/C750
6.31kN Yield	7.91kN Yield	8.37kN Yield

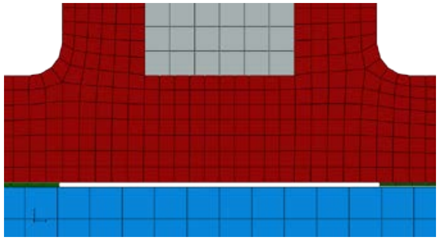
- ***Consistent and repeatable cohesive failures observed***

DESIGN TOOL & 3D Simulations



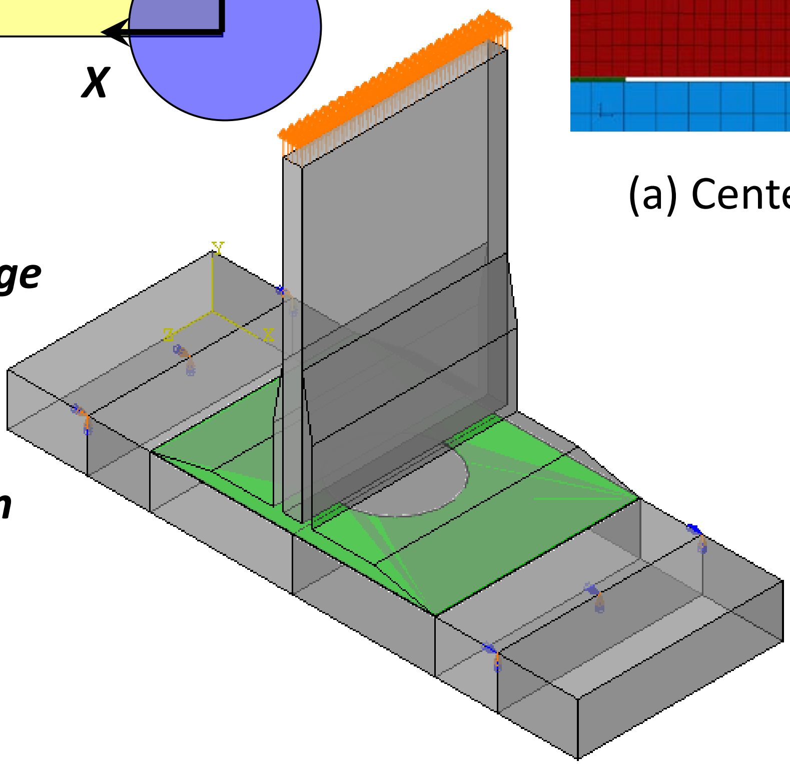


(a) Edge/Right Disbond



(a) Center Disbond

- ***Use Experimentally Validated Simulations (including flaws)***
- ***Predict Behavior of All possible damage locations***
- ***Obtain a Design Space , 3D - Performance Surfaces!***
- ***Develop Design Charts for easy use (in the field !)***



Progress: Technical Accomplishments/Results DESIGN TOOL & 3D Simulations